

COATINGS. ENAMELS

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DIFFUSION PROCESSES IN FIRING WILLEMITE GLAZE ON QUARTZ GLASS CERAMICS

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Diffusion processes occurring at the boundary between willemite glass-ceramic glaze and quartz glass ceramics are considered. Formation of a transitional contact zone between glaze and quartz glass ceramics is experimentally established, which ensures the formation of a strong bond of the coating to the substrate. The extent of the contact zone and the concentration distribution of components in this zone are determined using the method of layer-by-layer pickling and x-ray-fluorescent analysis. Coefficients of mutual diffusion of potassium and silicon ions are calculated for the glaze firing conditions.

Diffusion processes have an important role in glazing of ceramic articles, since they provide for the formation of intermediate layers at the glaze – substrate interface and facilitates strong adhesion of coating to ceramics [1, 2]. These processes acquire special significance in the case of insufficient coordination of thermal expansion coefficients of glaze and the substrate, which is the reason for the emergence of high thermal stresses and coating defects (crackle, chips) [3].

The purpose of our study was to investigate the diffusion processes in firing of alkali-resistant willemite glass-ceramic glaze deposited on quartz glass ceramic (“cersil”) produced by the Simvol JSC (Vladimir Region) [4]. Fritted vitreous glaze of the $K_2O - ZnO - TiO_2 - SiO_2$ system was deposited on the surface of quartz glass ceramics by immersion or casting and fired according to a two-stage procedure with exposures at temperatures of 1280°C (stage I: spreading of glaze) and 1050–1150°C (stage II: crystallization of coating). In the course of firing, a finely disperse volumetric glass-ceramic structure is formed in the glaze, which consists of willemite crystals and willemite-based solid solutions, zinc titanates, rutile, and a residual vitreous phase. The glaze coating forms strong adhesion to the substrate without crackle, scaling, or other defects.

The contact zone arising in the course of glaze firing was studied using the method of layer-by-layer pickling. The studies were performed in quartz glass-ceramic samples of diameter 40 mm coated on one side with a glaze layer 150 μm thick. Layer-by-layer pickling was carried out in a

solution of hydrofluoric acid. The lateral and bottom surfaces of the sample in pickling were protected by a polymer coating.

The thickness of a pickled layer $\Delta\delta_i$ (μm) was found from the formula

$$\Delta\delta_i = \frac{\Delta g_i \times 10^4}{\rho S_{\text{sam}}},$$

where Δg_i is the difference of the sample mass before and after pickling, g; ρ is the glaze density, g/cm³; S is the surface area of the sample, cm².

For the samples studies $\rho_{\text{gl}} = 3.415$ g/cm³, $S_{\text{sam}} = 12.56$ cm².

The chemical composition of the sample surface subjected to layer-by-layer pickling was determined by x-ray fluorescence analysis on a VRA-30 spectrometer under a voltage of 320 kV and current strength 15 μA. The content of SiO_2 , ZnO , TiO_2 , and K_2O was calculated based on the intensity of x-ray fluorescence lines of the respective elements (Si, Zn, Ti, and K) using the graduation dependence

$$I = f(w),$$

where I is the fluorescence intensity, pulses/s; w is the mass content of the component, %.

Based on the data obtained, the component concentration profiles were constructed for a cross-section of glazed sample (Fig. 1).

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Analysis of the concentration profiles indicates that a transitional contact zone 70–75 μm wide is formed between the glaze and quartz glass ceramic under firing. The contact zone is mainly formed due to diffusion of potassium ions, which penetrate into quartz glass ceramics to a depth of 20–25 μm , and silicon, which diffuses from the substrate into the glaze to a depth up to 50 μm . Zinc ions are virtually absent beyond line zero (initial boundary before firing), and titanium ions penetrate into quartz ceramics to a depth not more than 5 μm . Variations in the content of zinc and titanium oxides in the boundary glaze layer (before line zero) is due not to their diffusion, but to a modification of the content of silica in this layer.

To estimate the diffusion mobility of potassium and silicon, coefficients of mutual diffusion were calculated for these components based on the concentration profiles obtained. Since not only the concentration of a component, but also its gradient, becomes modified in the contact zone, the diffusion coefficient depends on the content of the component. Accordingly, to calculate the diffusion coefficient D for the components, one should use the second Fick law equation for a nonstationary flow:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial \delta} \left(D \frac{\partial w}{\partial \delta} \right),$$

where w is the mass content of material diffusing; δ is the cross-section coordinate; t is the time.

It is difficult to solve this equation directly; however, using the Boltzman – Matano method makes it possible to reduce it to an ordinary differential equation, whose integration with known initial and boundary conditions can be done rather simply [5]. The method involves introducing a new variable λ , which is related to δ and t by the relationship

$$\lambda = \frac{\delta}{\sqrt{t}}.$$

Solving the second Fick law equation with regard to D yields:

$$D = -\frac{1}{2} \frac{d\lambda}{dw} \int_0^w \lambda dw.$$

Substituting $\lambda = \frac{\delta}{\sqrt{t}}$ into this expression, we obtain

$$D = -\frac{1}{2t} \frac{d\delta}{dw} \int_0^w x dw.$$

If the diffusion coefficient does not depend on concentration, the amount of material leaving one half plane is equal to the quantity of material arriving into the other half plane. In this case the position of a boundary passing via line zero ($\delta = 0$) remains constant at any time moment. If the diffusion coefficient depends on concentration, then the amount of ma-

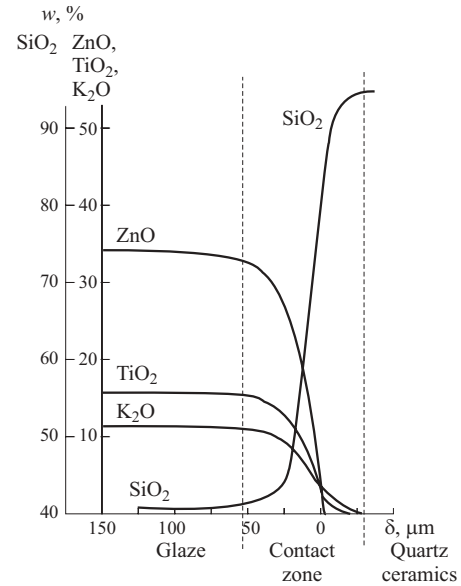


Fig. 1. Concentration distributions of components in a cross section of glazed quartz glass ceramics.

terial leaving one half plane is not equal to the amount of material arriving at the other half plane. To preserve this equality, the boundary has to be shifted to the position $\delta \neq 0$. The new boundary (the Matano boundary) can be determined based on the condition

$$\int_0^{w_m} \delta dw = - \int_{w_m}^{w_0} \delta dw, \quad \text{or} \quad \int_0^{w_0} \delta dw = 0.$$

Calculations show that the Matano boundary in the case considered is shifted from line zero to 5 μm toward the glaze, the potassium diffusion coefficient varies within the limits of $(2 - 10) \times 10^{-10}$, that of silicon varies within the limits of $(1.4 - 1.5) \times 10^{-10}$ or for $-\log D$ in the limits of 8.98–9.65 and 9.81–9.85, respectively (Table 1).

TABLE 1

Cation	Distance from Matano boundary, μm	Mass content of component, %	$D, 10^{-10} \text{ cm}^2/\text{sec}$	$-\log D$
K^+	20	10.2	10.4	8.98
	10	9.5	5.5	9.27
	5	8.5	4.0	9.40
	0	7.0	2.6	9.56
	-5	5.0	2.3	9.64
	-10	3.5	2.4	9.60
	-20	1.9	2.8	9.65
Si^{4+}	20	43.5	1.4	9.85
	10	44.0	1.4	9.85
	5	49.0	1.4	9.85
	0	65.5	1.1	9.97
	-5	72.0	1.4	9.85
	-10	90.0	1.5	9.81

TABLE 2

Ion	Heterodiffusion coefficient (1280°C), 10^{10} cm ² /sec		Chemical composition of melt	Self-diffusion coefficient (1200°C), cm ² /ses	Published source
	glaze	contact zone			
K ⁺	10.4	2.6	K ₂ O · 2SiO ₂	$3.9 \cdot 10^{-7}$	[7]
Si ⁴⁺	1.4	1.4	16.7K ₂ O · 16.7MgO · 66.6SiO ₂	$5.2 \cdot 10^{-6}$	[8]
			K ₂ O · 2SiO ₂	$5.4 \cdot 10^{-8}$	[7]

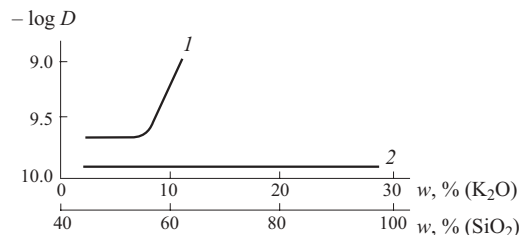


Fig. 2. Dependences of $-\log D$ for potassium (1) and silicon (2) ions on mass content of oxides.

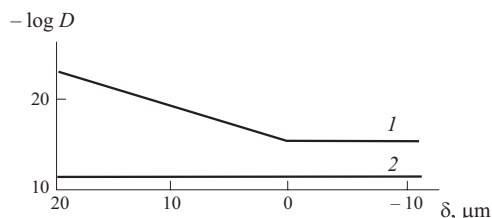


Fig. 3. Variation of $-\log D$ for potassium (1) and silicon (2) ions versus thickness of the glaze – quartz glass ceramics contact zone.

A correlation of the diffusion parameters indicates that potassium has a higher diffusion mobility than silicon. This agrees with the concept of the position of the elements considered in the glass structure: potassium ions are typical structure modifiers ensuring transport processes in glass, and silicon is a glass-forming component that is a part of a strongly bonded silicon-oxygen glass skeleton [6].

A correlation of the obtained values of diffusion coefficients with published data (Table 2) indicates that diffusion mobility in the glaze – quartz glass-ceramic system is lower than self-diffusion of these components in silicate melts. This observation correlates with the data supplied by certain authors that heterodiffusion requires more energy than self-diffusion, whereas the geometric parameters (ion size) do not have a determining role [9]. Another reason for the difference observed in the diffusion coefficients of the components in the case considered (heterodiffusion) from the published data (self-diffusion) is that the glaze and the contact zone are multiphase structures with a substantial amount of the vitreous phase. Its presence increases the apparent viscosity of the system and, accordingly, decreases the diffusion mobility of the cations.

The experimental data obtained (Table 2) were used to construct dependences of D on the mass content of the component (Fig. 2) and the profiles of D variation in the contact zone on the glaze – quartz glass-ceramic interface (Fig. 3). It can be seen that the potassium diffusion coefficient in an area with a low content of K₂O (up to 8%) does not depend on the content of potassium oxide. For higher contents of K₂O a concentration dependence of D is identified, which indicates an increase in the diffusion mobility of the cation. Accordingly, the potassium diffusion coefficient varies across a section of the glaze layer (a high content of K₂O) and does not vary in quartz glass ceramics (a low or impurity content of K₂O). The diffusion coefficient of silicon for the area, in which the content of SiO₂ was investigated, does not depend on the content of the component and remains constant over the whole cross-section of the sample.

The studies performed established that a contact zone 70 – 75 μm thick emerges in firing of glass-ceramic glaze deposited on quartz glass ceramics, which is reflected in the gradient of chemical composition. The formation of this zone is mainly due to mutual diffusion of potassium (from glaze) and silicon (from the substrate). Formation of a contact zone together with other factors facilitates strong adhesion of glaze to quartz glass ceramics.

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